

# Uses of Lime at Low Cost in Controlling SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>(v)/H<sub>2</sub>SO<sub>4</sub>(l) Emission

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## Summary

Due to complex cyclical influences, including boiler soot blowing, a resulting continuous variation in the SO<sub>3</sub> concentration of the boiler gas is ominous and challenging in and of itself, particularly in high-sulfur service. Retrofitting of high-dust SCR can increase SO<sub>3</sub> generation and exacerbate any pre-existing SO<sub>3</sub> problem. SO<sub>3</sub> is generated both in the furnace, i.e. homogeneous/gas-phase interaction of SO<sub>2</sub> with atomic oxygen, and in the downstream, convective pass, i.e. temperature and tube-surface-area dependent, heterogeneous/catalytic oxidation of SO<sub>2</sub> by molecular oxygen. Below 600°F (316°C), SO<sub>3</sub> combines with H<sub>2</sub>O(v) to form H<sub>2</sub>SO<sub>4</sub>(v). Some of this gaseous acid condenses onto cold surfaces (T < 280°F, i.e. 138°C) and is also adsorbed onto gas-entrained fly ash. A simplistic, EPA-based, proportionality constant indicates that a nominal 0.7% of flue-gas SO<sub>2</sub> becomes oxidized to SO<sub>3</sub> by the boiler. But due to an array of factors, including the cyclically varying catalytic-oxidation influence of iron, i.e. iron oxide, (present in both the boiler tube surface material and in ash), a broad range of SO<sub>3</sub> concentration may be experienced daily. This is because:

- The rate of oxidation of SO<sub>2</sub> to SO<sub>3</sub> by iron oxides peaks at 1300°F, (704°C).
- Periodic, low-temperature, soot blowing with boiler gas at 1100 to 1600°F, i.e. 593 to 871°C, brings SO<sub>3</sub> formation to a peak by causing exposure of and enhancing the significant catalytic oxidation brought about by boiler tube metal.

Depending on the boiler type, slag tap or dry bottom boiler, coal composition and boiler operating conditions, the average SO<sub>2</sub>-to-SO<sub>3</sub> conversion rate in the boiler can range as high as 1.5%. Significant, additional, SO<sub>3</sub>-concentration increase is caused by high-dust SCR systems. Measured overall SO<sub>3</sub>-conversion rates are 1.0 to 4.5%, depending mainly on catalyst type and operating temperature. In several power plants in Germany, H<sub>2</sub>SO<sub>4</sub> concentration of 140mg/Nm<sup>3</sup> (32 ppm) is measured downstream of high-dust SCR. There are results from 3.3% sulfur, residual oil fired power stations wherein H<sub>2</sub>SO<sub>4</sub> concentrations of 200 mg/Nm<sup>3</sup> (45 ppm) are measured upstream of high-dust SCR and 330 mg/Nm<sup>3</sup> (74 ppm) downstream. To eliminate or minimize the sulfuric acid aerosol plume opacity, several reagents have been applied by injection on a trial basis but without great success. Only ammonia injection in the economizer has given adequate results, but acid aerosol is substituted by a visible ammonium salt plume since, to achieve a high SO<sub>3</sub> removal efficiency, excess ammonia has to be injected.

Continuous variation in the degree of boiler tube fouling can, through influence on rate of catalyzed  $\text{SO}_3$  generation, created significant cyclical episodes impacting the air preheater. By model study the complex catalytic influence on  $\text{SO}_2$  oxidation of the iron oxide coated surface of the exposed superheater tube metal has been emphasized: operation with a clean superheater has been shown to result in 20 ppm flue-gas  $\text{SO}_3$  concentration, and a heavily fouled superheater yielded 32 ppm, while with a moderately fouled superheater there was a maximum concentration: 70 ppm!! Moreover, even in the absence of a high-dust SCR facility some high-sulfur units have had a significant history of air preheater fouling associated with such high levels of boiler generation of  $\text{SO}_3$ .

Hydrated lime injection techniques have been widely investigated in the field to achieve dry sorption of  $\text{SO}_3$ , this necessarily applied upstream of fly ash collection in the absence of an FGD system.

Comparative field test results are reviewed and guidelines are presented in detail. Lime-using dry and semi-dry scrubbers are a routine means of controlling  $\text{SO}_3$ , removing it even more efficiently than  $\text{SO}_2$ , this without water saturating the gas. Wet scrubbers quench/cool and water-saturate the flue gas so rapidly that a large proportion of inlet  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4(\text{v})$ , nominally one half of the total amount, is hydrated to sub-micron sulfuric acid mist,  $\text{H}_2\text{SO}_4(\text{l})$ , the balance being rapidly absorbed in the scrubbing medium.